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TITLE: AMINO COCONDENSATION RESIN AND ITS PRODUCTION

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ABSTRACT:

PURPOSE: To obtain an amino cocondensation resin excellent in resistances to water and boiling water, weatherability, and adhesive properties by producing a specific deriv. of a cocondensate of an amino compd., a phenol, and an aldehyde (donor).

CONSTITUTION: This resin is a sulfomethylation product of a cocondensate of an amino compd. (e.g. urea), a phenol (e.g. phenol), and an aldehyde (donor) (e.g. HCHO) and is produced pref. by cocondensing the amino compd. and/or an amino compd.-aldehyde condensate with the phenol and/or a phenol-aldehyde condensate in the absence or presence of the aldehyde (donor) under such a condition that a sulfomethylating agent (e.g. sodium sulfite) is added before, during, or after the condensation and reacted.

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 DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Amino ** by which this invention is used for adhesives, such as wood, paper, rubber, synthetic resin, inorganic and organic fiber, and a metal, a binder, an impregnant, a coating agent, a coating vehicle, etc. is related with condensation resin.

[0002]

[Description of the Prior Art] Conventionally, an amino resin like a urea-resin, melamine resin, and a urea melamine copolycondensation resin was cheap, and in order to carry out heating hardening at low temperature comparatively, it has been used in large quantities as adhesives, such as a plywood and particle board. However, the amino resin adhesive had the fault from which a deck watertight luminaire, boiling-proof nature, and weatherability often start an adhesive agent to the tree-species wood of a difficulty adhesive property bad. For this reason, when a deck watertight luminaire, boiling-proof nature, and weatherability are demanded especially, the resol type phenol system resin has been used instead of an amino resin as adhesives for wood from the former. When using a resol type phenol system resin as adhesives for plywoods, it compares with an amino resin. However, since [that price is high and] a curing temperature is comparatively high, The time of the xeransis for lowering the water content of the veneer as a last process of adhesion, in order for a blowout phenomenon to happen and to prevent this, in case water will serve as a steam and will escape in *****, if the water content of the veneer is high is needed. Moreover, the store stability of a resin was bad and there was a fault, like a resin carries out [pH] the separation freezing below by neutrality. In order to improve these faults, while a copolycondensation is carried out to an amino ***** monomer, a phenol, and an aldehyde and a manufacturing cost is reduced, the method of making the curing temperature of a resin fall and aiming at the enhancement in a deck watertight luminaire, boiling-proof nature, weatherability, and adhesive power further is tried variously.

[0003]

[Problem(s) to be Solved by the Invention] However, the neglect stability was inferior in the copolycondensation object of an amino ***** monomer and a phenols, and its compatibility with water was bad, and since the resin carried out the separation freezing below by neutrality, it had the fault which cannot use acid catalysts, such as an ammonium chloride. Therefore, amino ** of offering the aldehyde copolycondensation field resin of the stable amino ***** monomer and stable phenols which do not carry out the separation freezing even if it adds an acid catalyst and by which a deck watertight luminaire, boiling-proof nature, weatherability, and adhesive power were improved was the very important technical technical problem of condensation resin.

[0004]

[Means for Solving the Problem] If this invention person makes a sulfo methyl group exist in the copolycondensation object with an amino ***** monomer, a phenols, an aldehyde, and/or an aldehyde donator The copolycondensation object with a good neglect stability is obtained, and the compatibility with water increases, and an acidity side also becomes stable. When adding the acid catalyst and/or the aldehyde curing agent, heating hardening was comparatively carried out at low temperature, a deck watertight luminaire, boiling-proof nature, and weatherability were excellent, and it found out that ordinary temperature or the hardening resin which has a strong adhesive property to wood etc. was obtained. this invention as a means for solving the aforementioned conventional technical problem Namely, an amino ***** monomer, and/or amino ***** and an aldehyde condensate, It is what amino ** which is the sulfo methylation object of the copolycondensation object with a phenols and/or a phenols and an aldehyde condensate, an aldehyde, and/or an aldehyde donator provides with condensation resin. Condensation resin the above-mentioned amino ** An amino ***** monomer Amino ***** and an aldehyde condensate, a phenols and/or a phenols, and an aldehyde condensate under presence of an aldehyde and/or an aldehyde donator and/or, or by carrying out a copolycondensation without presence It is manufactured by the technique of carrying out the addition reaction of the sulfo methylation agent, in manufacturing the aldehyde copolycondensation field of an amino ***** monomer and a phenols in front of this condensation reaction or in a condensation reaction, and after a condensation reaction. this invention is explained in detail below.

[0005] In [amino ***** monomer" this invention, an amino ***** monomer means a kind of amino *****, or two sorts or more of mixture which carries out a condensation reaction to aldehydes, such as a carbamide and/or an amino azine, and generates the resin of hardenability, and a urea, thiourea, a melamine, a thio melamine, a dicyandiamide, guanidine,

a guanamine, acetoguanamine, benzoguanamine, 2, the 6-diamino -1, 3-diazine, etc. are illustrated.

[0006] The phenols in a [phenols] this invention means a kind of a monohydric phenol and/or a polyhydric phenol, or two sorts or more of mixture. As a monohydric phenol here Alkylphenols, such as o-cresol, m-cresol, p-cresol, ethylphenol, iso-propyl phenol, a xylol, 3, 5-xylol, butylphenol, t-butylphenol, and a nonyl phenol, o-fluorophenol, m-fluorophenol, p-fluorophenol, o-chlorophenol, m-chlorophenol, p-chlorophenol, o-***** phenol, m-***** phenol, p-***** phenol, o-iodine phenol, m-iodine phenol, p-iodine phenol, ortho aminophenol, m-aminophenol, para aminophenol, ortho nitrophenol, m-nitrophenol, p-nitrophenol, a 2, 4-dinitrophenol, 2, 4, 1 ** phenols, such as 1 ** phenol substitution products, such as 6-trinitrophenol, and a naphthol, are illustrated. Moreover, as a polyhydric phenol, polyhydric phenols, such as a resorcinol, an alkyl resorcinol, pyrogallol, a catechol, an alkyl catechol, hydroquinone, alkyl hydroquinone, a phloroglucine, a bisphenol, and dihydroxy naphthalene, are illustrated. A resorcinol or an alkyl resorcinol is desirable among these polyhydric phenols, and especially a desirable thing is an alkyl resorcinol with the reaction rate quicker than a resorcinol with an aldehyde. As the above-mentioned alkyl resorcinol For example, 5-methyl resorcinol, 5-ethyl resorcinol, 5-propyl resorcinol, a 5-n-butyl resorcinol, 4, 5-dimethyl resorcinol, 2, 5-dimethyl resorcinol, 4, 5-diethyl resorcinol, 2, 5-diethyl resorcinol, 4, 5-dipropyl resorcinol, There are 2, 5-dipropyl resorcinol, a 4-methyl-5-ethyl resorcinol, a 2-methyl-5-ethyl resorcinol, a 2-methyl-5-propyl resorcinol, 2 and 4, a 5-trimethyl resorcinol, 2 and 4, a 5-triethyl resorcinol, etc. Since the polyhydric-phenol mixture obtained by dry distillation of the Estonia ** oil shale contains the various high alkyl resorcinols of reactivity besides 5 ***** resorcinol so much cheaply, it is the most desirable polyhydric-phenol raw material to this invention.

[0007] With the aldehyde and/or aldehyde donator in a [aldehyde donator] this invention An aldehyde and/or the compound which will carry out generation supply of the aldehyde if it decomposes are meant. Formalin, formaldehyde, a paraformaldehyde, a trioxane, an acetaldehyde, a propionaldehyde, a polyoxymethylene, a trichloroacetic aldehyde, a hexamethylenetetramine, a furfural, glyoxal, n-butyraldehyde, a caproaldehyde, Kinds, such as an allyl-compound aldehyde, the Benz aldehyde, a crotonaldehyde, an acrolein, a tetrapod oxy-methylene, a phenylacetaldehyde, o-torr aldehyde, and a salicylaldehyde, or two sorts or more of mixture is illustrated.

[0008] As a sulfo methylation agent used in a [sulfo methylation agent] this invention, hydroxy alkane sulfonic acids, such as a water-soluble sulfite with quaternary amines, such as a sulfurous acid, a pile sulfurous acid or a meta-pile sulfurous acid, alkali metal or a trimethylamine, and benzyl trimethylammonium, or the fourth class ***** and hydroxy methanesulfon acid chloride obtained by the reaction of these water-soluble sulfites and aldehydes, are illustrated. [whether this water-soluble sulfite reacts with the methylol machine of the copolycondensation object (C) with amino ***** and the initial condensate (A) of an aldehyde, a phenols and/or a phenols, and the initial condensate (B) of an aldehyde, and generates a sulfo methyl group, and] Or in case the initial condensate (B) of above-mentioned first stage condensate (A) or a copolycondensation object (C) is made to condense, it reacts with the aldehyde which exists in the system of reaction first, and a hydroxy alkane sulfonate is formed, subsequently it reacts with amino ***** or a phenol, and a sulfoalkyl machine is formed. Therefore, hydroxy alkane sulfonates, such as hydroxy methanesulfon acid chloride, can also be used as a sulfo methylation agent instead of a water-soluble sulfite.

[0009] In a [complexing-agent] this invention, when a part or all of a phenols that is used is a polyhydric phenol in the case of the copolycondensation reaction of an initial condensate (C) in the case of condensation of an initial condensate (B), you may add the complexing agent which mitigates the reactivity of a polyhydric phenol and an aldehyde. The compound which has a ketone group or an amide group etc. which has complexing organization potency to the hydroxyl of a polyhydric phenol as such a complexing agent is raised, for example, an acetone, a caprolactam, etc. are illustrated, and especially an acetone is a desirable complexing agent. Although especially a limit does not have the addition of a complexing agent, about 0.4-0.8 mols of complexing agents are usually desirable to the polyhydric phenol of one mol.

[0010] In a [third-component] this invention in addition to an amino ***** monomer, a phenols, an aldehyde donator, a sulfo methylation agent, a condensation catalyst, and a complexing agent as a third component a request -- if -- toluene, a xylene, a cumarone, a cyclohexanone, cashew oil, tannin, *****, a shellac, rosin, or a rosin derivative -- Kinds, such as a petroleum resin, a methanol, ethanol, an isopropanol, n-butanol, an isobutanol, ethylene glycol, a diethylene glycol, a polyethylene glycol, a glycerol, furfuryl alcohol, the linseed oil, tung oil, and castor oil, or two sorts or more It does not interfere, even if it adds and denaturalizes among a reaction or after a reaction end as a copolycondensation agent or a modifier at the time of reaction start of condensation or a copolycondensation.

[0011] Although the indifferent water is used as a solvent at the time of the reaction of a [solvent] this invention, if required, the addition use of that water fusibility organic solvents, such as ketones, such as alcohols, such as a methanol, ethanol, an isopropanol, n-butanol, ethylene glycol, a diethylene glycol, and a polyethylene glycol, an acetone, and a methyl ethyl ketone, are still independent or two or more sorts of mixture can be carried out. While an acetone etc. is a solvent, it acts also as a complexing agent of a polyhydric phenol like an alkyl resorcinol, and brings a quieter reaction.

[0012] In a [condensation-reaction and sulfo methylation reaction] this invention, the sulfo methylation object of the copolycondensation object with an amino ***** monomer, a phenols, an aldehyde, and/or an aldehyde donator is obtained by the following technique.

1. the initial condensate (SA) of sulfo methylation which carried out the condensation reaction of an amino ***** monomer, an aldehyde, and/or the aldehyde donator to the bottom of presence of a sulfo methylation agent, or carried out sulfo methylation of the initial condensate (A) with an amino ***** monomer, an aldehyde, and/or an aldehyde donator by the

sulfo methylation agent, and a phenols -- the bottom of presence of an aldehyde and/or an aldehyde donator -- or carry out a copolycondensation without presence

2. the initial condensate (SA) of sulfo methylation which carried out the condensation reaction of an amino ***** monomer, an aldehyde, and/or the aldehyde donator to the bottom of presence of a sulfo methylation agent, or carried out sulfo methylation of the initial condensate (A) with an amino ***** monomer, an aldehyde, and/or an aldehyde donator by the sulfo methylation agent, and the initial condensate (B) with a phenols, an aldehyde, and/or an aldehyde donator -- the bottom of presence of an aldehyde and/or an aldehyde donator -- or

3. the initial condensate (A) with an amino ***** monomer, an aldehyde, and/or an aldehyde donator, and a phenols -- the bottom of presence of a sulfo methylation agent -- and the bottom of presence of an aldehyde and/or an aldehyde donator -- or carry out a copolycondensation without presence

4. It is under presence of an aldehyde and/or an aldehyde donator, or carry out without presence the copolycondensation of the initial condensate (SB) of sulfo methylation which carried out sulfo methylation of a phenols, an aldehyde and/or an aldehyde donator, and the initial condensate (B) by the sulfo methylation agent.

5. the initial condensate (A) with an amino ***** monomer, an aldehyde, and/or an aldehyde donator, and the initial condensate (B) with a phenols, an aldehyde, and/or an aldehyde donator -- the bottom of presence of a sulfo methylation agent -- and the bottom of presence of an aldehyde and/or an aldehyde donator -- or carry out a copolycondensation without presence

6. [whether Condensation Reaction is Carried Out under Presence of Amino ***** Monomer, Aldehyde and/or Aldehyde Donator, and Sulfo Methylation Agent, and] The initial condensate (A) with an amino ***** monomer, an aldehyde, and/or an aldehyde donator by the sulfo methylation agent [whether the condensation reaction of the initial condensate (SA) of sulfo methylation, the phenols, the aldehyde, and/or aldehyde donator which carried out sulfo methylation is carried out under presence of a sulfo methylation agent, and] It is under presence of an aldehyde and/or an aldehyde donator, or the copolycondensation of the initial condensate (SB) of sulfo methylation which carried out sulfo methylation of a phenols, an aldehyde and/or an aldehyde donator, and the initial condensate (B) by the sulfo methylation agent is carried out without presence.

7. Make an amino ***** monomer, a phenols, an aldehyde, and/or an aldehyde donator live together, and carry out a copolycondensation under presence of a sulfo methylation agent.

It can add and a sulfo methylation agent can be made to react after a reaction before a reaction or in a reaction in each above-mentioned condensation or an above-mentioned copolycondensation reaction.

[0013] In the above-mentioned copolycondensation reaction, although the addition proportion of an amino ***** monomer and a phenols is arbitrary, it is usually added 0.01-100 mols of phenolss to one mol of amino ***** monomers. In the above-mentioned condensation or a copolycondensation reaction, it sets for an amino ***** reaction. in the case of amino ***** and the initial condensate (A) of an aldehyde The addition of the aldehyde to one mol of amino ***** monomers, and/or an aldehyde donator Usually, the about 0.5 to 2.0 times [of the number of reactant amino groups which can react with the aldehyde contained in one mol of these ***** system compound monomers] number of mols is suitable. For example, in the case of a urea, in the case of 1.0-3.0 mols and a melamine, the addition of an aldehyde and/or an aldehyde donator is about 1.5-6 mols.

[0014] When condensation resin is used for amino ** of this invention as an object for adhesives, a urea and/or a melamine are usually used as an amino ***** monomer. When using both a urea and a melamine, 1-6 mols of ureas are usually added to one mol of melamines, and an aldehyde and/or about 1-10 mols of aldehyde donators are added. The addition of an aldehyde [as opposed to one mol of phenolss in the case of a phenols and the initial condensate (B) of an aldehyde] and/or an aldehyde donator is 0.2-3 mols. Moreover, 150/[1/100 of the number of sum mols of an amino ***** monomer and a phenols -] 100 considerable amount is usually suitable for the addition of a sulfo methylation agent.

[0015] In condensation of the above-mentioned initial condensate (A) and an initial condensate (B), or the copolycondensation reaction of an initial condensate (A) and an initial condensate (B), from the beginning of a condensation reaction, the whole quantity, in addition ** of an aldehyde and/or an aldehyde donator are good, and they may carry out split addition or per-continuum instillation.

[0016] Moreover, in the above-mentioned condensation or a copolycondensation reaction, a reaction is usually carried out in the domain of pH 4-12, and a catalyst or a pH regulator is added if needed. As these catalysts or a pH regulator, it is inorganic and organic an acid, alkali, or those salts, and caustic alkali of sodium, a caustic potash, a barium hydroxide, a calcium hydroxide, sodium carbonate, lime, ammonia, a trimethylamine, a triethylamine, a hexamethylenetetramine, a pyridine, a hydrochloric acid, oxalic acid, formic acid, an acetic acid, a lactic acid, a way acid, etc. are illustrated. Moreover, the addition of a catalyst or a pH regulator is usually several percent or less of an amino ***** monomer or a phenols. The reaction temperature of the above-mentioned condensation or a copolycondensation is usually 50-120 degrees C, and is performed about 0.5 to 48 hours. Furthermore, if required in addition to a catalyst or a pH regulator, a solvent, a complexing agent, and a third component can be added and this condensation reaction can be made to carry out in the above-mentioned condensation or a copolycondensation reaction.

[0017] if a part or all of a phenols that is added in this invention is made into a polyhydric phenol and it is [the copolycondensation object (C) with the high reactivity with an aldehyde is obtained and] required -- an acid catalyst and/or an aldehyde curing agent -- adding -- ordinary temperature -- or it hardens by low-temperature heating comparatively, and

hardening resin is excellent in a deck watertight luminaire, boiling-proof, and weatherability, and has strong adhesive ability, such as wood To such a purpose, a resorcinol and the sulfo methylation object (SC) of a copolycondensation object (C) which especially the alkyl resorcinol is effective, uses together an alkyl resorcinol independent or 1 ** phenol, and an alkyl resorcinol as a phenols, carries out a copolycondensation to an amino ***** monomer, and/or amino ***** and the initial condensate of an aldehyde (A), and is obtained are especially desirable. Rather than it carries out the addition copolycondensation of both simultaneously with a monomer, in case a copolycondensation object (C) is manufactured, when using together 1 ** phenol and a polyhydric phenol (1) A polyhydric phenol under an aldehyde or aldehyde donator presence to the initial condensate of 1 ** phenolaldehyde which carried out sulfo methylation Or the initial condensate (SB), the amino ***** monomer, and/or amino ***** and the aldehyde condensate which carried out the copolycondensation without presence (A) under an aldehyde and/or aldehyde donator presence or [whether a copolycondensation is carried out without presence, and] (2) The initial condensate (SB) of 1 ** phenolaldehyde, the amino ***** monomer, and/or amino ***** and the aldehyde condensate (A) which carried out sulfo methylation under an aldehyde and/or aldehyde donator presence in or the copolycondensation object (SC) condensed without presence Furthermore, although there is the technique of being under an aldehyde and/or aldehyde donator presence, or carrying out the copolycondensation of the polyhydric phenol without presence etc., since a more stable copolycondensation object is obtained, the former technique (1) is the desirable copolycondensation technique.

[0018] Generally, it is obtained that a product [carry / to the methylol machine produced in the condensate of a phenols and an aldehyde] is more stable rather than it performs sulfo methylation to the methylol machine produced in the condensate of amino ***** and an aldehyde.

[0019] Heating hardening will be carried out if the acid catalyst 0.05 - 10 weight section, and the curing agent 0 which will consist of an aldehyde donator like para ***** if required - 50 weight section are added to amino ***** the phenols, and the aldehyde copolycondensation object (SC) 100 weight section by which sulfo methylation of the [hardening of initial copolycondensation object by which sulfo methylation was carried out] this invention was carried out. The heating hardening is performed at low temperature farther than the case (they are usually 1 minute / about 1mm at 125-140 degrees C in plywood adhesion) of hardening of resol type phenol resin, and they are usually 0.5 - 1 minute / about 1mm at 110-120 degrees C. If the curing agent which the reactivity with the aldehyde of this copolycondensation resin (SC) will be raised notably, and will consist of an aldehyde donator like para ***** if a polyhydric phenol like a resorcinol or an alkyl resorcinol exists in the phenols component of the copolycondensation resin (SC) with which sulfo methylation of this invention was carried out is added, it is not concerned with an acid and alkaline situation, but comes to be able to carry out a room temperature setting in large pH field. However, it is required to heat in the ordinary temperature [like a hexamethylenetetramine] whose aldehyde donator is, more than the decomposition temperature, in being stable. Moreover, in this invention, even if it adds an acid or alkaline curing catalyst in the case of hardening, it does not interfere. The acid or alkaline above-mentioned curing catalyst If it illustrates, an ammonium chloride, an ammonium sulfate, an ammonium acetate, an ammonium thiocyanate, imido sulfonic-acid ammonium, ammonium phosphate, an ammonium oxalate, a hexamethylenetetramine, ammonia, sodium acetate, a sodium phosphate, an aniline chloride, An ammonium sulfate, a hydrochloric acid, oxalic acid, formic acid, an acetic acid, a lactic acid, a way acid, and the carboxylates like oxalic acid dimethyl ester Organic halogenides, such as the acid-anhydrides [such as a maleic-acid anhydride and a phthalic-acid anhydride], specific-salt [of monochloroacetic acid], alpha, and alpha'-dichlorohydrin, There are urea adducts, such as a hydrochloride of aminess, such as an ethylamine hydrochloride and a triethanolamine hydrochloride, a salicylic-acid urea adduct, a stearin acid urea adduct, and an oenanthic-acid urea adduct, an N-trimethyl taurine, etc., and these may use together a kind or two sorts or more. If required in the case of hardening, furthermore, amino resins, such as 1 ** phenol system resin, a polyhydric-phenol system resin, a urea system resin, and a melamine system resin, Synthetic rubber, such as natural rubber and its derivative, a styrene butadiene rubber, acrylonitrile-butadiene rubber, chloroprene rubber, ethylene-propylene rubber, polyisoprene rubber, and isoprene-isobutylene rubber, The homopolymer of vinyl monomers, such as vinyl acetate, a propionic-acid vinyl, styrene, acrylic ester, methacrylic ester, acrylonitrile, an acrylic acid, a methacrylic acid, a maleic acid, a vinyl chloride, a vinylidene chloride, and a ***** pyridine Or two or more sorts of copolymers of these vinyl monomers, Emulsions, and ***** or the aqueous solutions of various synthetic resin, such as polyurethane, a polyamide, an epoxy resin, a butyral resin, polyethylene, polypropylene, a vinyl acetate-ethylene copolymer, a chlorinated polyethylene, chlorination polypropylene, and polyester, Moreover, water soluble polymers and natural gums, such as polyvinyl alcohol, a sodium alginate, a starch, a starch derivative, glue, gelatin, powdered blood, a methyl cellulose, a carboxymethyl cellulose, a hydroxyethyl cellulose, a polyacrylic acid, and a polyacrylamide, Furthermore, bulking agents, such as carbonic acid calcium, talc, plaster, carbon black, wood flour, walnut powder, coconut shell powder, a wheat flour, and rice powder, A pigment, a color, a flame retarder, a flame proofing agent, an insecticide, antiseptics, an antioxidant, an ultraviolet ray absorbent, DBP, DOP, Third components, such as plasticizers, such as a ***** acid ester system plasticizer like a dicyclohexyl free-wheel-plate rate and other tricresyl phosphate, may be added in this copolycondensation object (SC), and this copolycondensation object (SC) may be made to denaturalize by the copolycondensation, mixture, etc.

[0020]

[Function] Amino ** of this invention the sulfo methylation object (SC) of condensation resin (C), i.e., amino ***** , a phenols, and an aldehyde copolycondensation object

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[0005] In [amino ***** monomer" this invention, an amino ***** monomer means a kind of amino *****, or two sorts or more of mixture which carries out a condensation reaction to aldehydes, such as a carbamide and/or an amino azine, and generates the resin of hardenability, and a urea, thiourea, a melamine, a thio melamine, a dicyandiamide, guanidine,

a guanamine, acetoguanamine, benzoguanamine, 2, the 6-diamino -1, 3-diazine, etc. are illustrated.

[0006] The phenols in a [phenols] this invention means a kind of a monohydric phenol and/or a polyhydric phenol, or two sorts or more of mixture. As a monohydric phenol here Alkylphenols, such as o-cresol, m-cresol, p-cresol, ethylphenol, iso-propyl phenol, a xylenol, 3, 5-xyleneol, butylphenol, t-butylphenol, and a nonyl phenol, o-fluorophenol, m-fluorophenol, p-fluorophenol, o-chlorophenol, m-chlorophenol, p-chlorophenol, o-***** phenol, m-***** phenol, p-***** phenol, o-iodine phenol, m-iodine phenol, p-iodine phenol, ortho aminophenol, m-aminophenol, para aminophenol, ortho nitrophenol, m-nitrophenol, p-nitrophenol, a 2, 4-dinitrophenol, 2, 4, 1 ** phenols, such as 1 ** phenol substitution products, such as 6-trinitrophenol, and a naphthol, are illustrated. Moreover, as a polyhydric phenol, polyhydric phenols, such as a resorcinol, an alkyl resorcinol, pyrogallol, a catechol, an alkyl catechol, hydroquinone, alkyl hydroquinone, a phloroglucine, a bisphenol, and dihydroxy naphthalene, are illustrated. A resorcinol or an alkyl resorcinol is desirable among these polyhydric phenols, and especially a desirable thing is an alkyl resorcinol with the reaction rate quicker than a resorcinol with an aldehyde. As the above-mentioned alkyl resorcinol For example, 5-methyl resorcinol, 5-ethyl resorcinol, 5-propyl resorcinol, a 5-n-butyl resorcinol, 4, 5-dimethyl resorcinol, 2, 5-dimethyl resorcinol, 4, 5-diethyl resorcinol, 2, 5-diethyl resorcinol, 4, 5-dipropyl resorcinol, There are 2, 5-dipropyl resorcinol, a 4-methyl-5-ethyl resorcinol, a 2-methyl-5-ethyl resorcinol, a 2-methyl-5-propyl resorcinol, 2 and 4, a 5-trimethyl resorcinol, 2 and 4, a 5-triethyl resorcinol, etc. Since the polyhydric-phenol mixture obtained by dry distillation of the Estonia ** oil shale contains the various high alkyl resorcinols of reactivity besides 5 ***** resorcinol so much cheaply, it is the most desirable polyhydric-phenol raw material to this invention.

[0007] With the aldehyde and/or aldehyde donator in a [aldehyde donator] this invention An aldehyde and/or the compound which will carry out generation supply of the aldehyde if it decomposes are meant. Formalin, formaldehyde, a paraformaldehyde, a trioxane, an acetaldehyde, a propionaldehyde, a polyoxymethylene, a trichloroacetic aldehyde, a hexamethylenetetramine, a furfural, glyoxal, n-butyraldehyde, a caproaldehyde, Kinds, such as an allyl-compound aldehyde, the Benz aldehyde, a crotonaldehyde, an acrolein, a tetrapod oxy-methylene, a phenylacetaldehyde, o-torr aldehyde, and a salicylaldehyde, or two sorts or more of mixture is illustrated.

[0008] As a sulfo methylation agent used in a [sulfo methylation agent] this invention, hydroxy alkane sulfonic acids, such as a water-soluble sulfite with quaternary amines, such as a sulfurous acid, a pile sulfurous acid or a meta-pile sulfurous acid, alkali metal or a trimethylamine, and benzyl trimethylammonium, or the fourth class ***** and hydroxy methanesulfon acid chloride obtained by the reaction of these water-soluble sulfites and aldehydes, are illustrated. [whether this water-soluble sulfite reacts with the methylol machine of the copolycondensation object (C) with amino ***** and the initial condensate (A) of an aldehyde, a phenols and/or a phenols, and the initial condensate (B) of an aldehyde, and generates a sulfo methyl group, and] Or in case the initial condensate (B) of above-mentioned first stage condensate (A) or a copolycondensation object (C) is made to condense, it reacts with the aldehyde which exists in the system of reaction first, and a hydroxy alkane sulfonate is formed, subsequently it reacts with amino ***** or a phenol, and a sulfoalkyl machine is formed. Therefore, hydroxy alkane sulfonates, such as hydroxy methanesulfon acid chloride, can also be used as a sulfo methylation agent instead of a water-soluble sulfite.

[0009] In a [complexing-agent] this invention, when a part or all of a phenols that is used is a polyhydric phenol in the case of the copolycondensation reaction of an initial condensate (C) in the case of condensation of an initial condensate (B), you may add the complexing agent which mitigates the reactivity of a polyhydric phenol and an aldehyde. The compound which has a ketone group or an amide group etc. which has complexing organization potency to the hydroxyl of a polyhydric phenol as such a complexing agent is raised, for example, an acetone, a caprolactam, etc. are illustrated, and especially an acetone is a desirable complexing agent. Although especially a limit does not have the addition of a complexing agent, about 0.4-0.8 mols of complexing agents are usually desirable to the polyhydric phenol of one mol.

[0010] In a [third-component] this invention in addition to an amino ***** monomer, a phenols, an aldehyde donator, a sulfo methylation agent, a condensation catalyst, and a complexing agent as a third component a request -- if -- toluene, a xylene, a cumarone, a cyclohexanone, cashew oil, tannin, *****, a shellac, rosin, or a rosin derivative -- Kinds, such as a petroleum resin, a methanol, ethanol, an isopropanol, n-butanol, an isobutanol, ethylene glycol, a diethylene glycol, a polyethylene glycol, a glycerol, furfuryl alcohol, the linseed oil, tung oil, and castor oil, or two sorts or more It does not interfere, even if it adds and denaturalizes among a reaction or after a reaction end as a copolycondensation agent or a modifier at the time of reaction start of condensation or a copolycondensation.

[0011] Although the indifferent water is used as a solvent at the time of the reaction of a [solvent] this invention, if required, the addition use of that water fusibility organic solvents, such as ketones, such as alcohols, such as a methanol, ethanol, an isopropanol, n-butanol, ethylene glycol, a diethylene glycol, and a polyethylene glycol, an acetone, and a methyl ethyl ketone, are still independent or two or more sorts of mixture can be carried out. While an acetone etc. is a solvent, it acts also as a complexing agent of a polyhydric phenol like an alkyl resorcinol, and brings a quieter reaction.

[0012] In a [condensation-reaction and sulfo methylation reaction] this invention, the sulfo methylation object of the copolycondensation object with an amino ***** monomer, a phenols, an aldehyde, and/or an aldehyde donator is obtained by the following technique.

1. the initial condensate (SA) of sulfo methylation which carried out the condensation reaction of an amino ***** monomer, an aldehyde, and/or the aldehyde donator to the bottom of presence of a sulfo methylation agent, or carried out sulfo methylation of the initial condensate (A) with an amino ***** monomer, an aldehyde, and/or an aldehyde donator by the

sulfo methylation agent, and a phenols -- the bottom of presence of an aldehyde and/or an aldehyde donator -- or carry out a copolycondensation without presence

2. the initial condensate (SA) of sulfo methylation which carried out the condensation reaction of an amino ***** monomer, an aldehyde, and/or the aldehyde donator to the bottom of presence of a sulfo methylation agent, or carried out sulfo methylation of the initial condensate (A) with an amino ***** monomer, an aldehyde, and/or an aldehyde donator by the sulfo methylation agent, and the initial condensate (B) with a phenols, an aldehyde, and/or an aldehyde donator -- the bottom of presence of an aldehyde and/or an aldehyde donator -- or

3. the initial condensate (A) with an amino ***** monomer, an aldehyde, and/or an aldehyde donator, and a phenols -- the bottom of presence of a sulfo methylation agent -- and the bottom of presence of an aldehyde and/or an aldehyde donator -- or carry out a copolycondensation without presence

4. It is under presence of an aldehyde and/or an aldehyde donator, or carry out without presence the copolycondensation of the initial condensate (SB) of sulfo methylation which carried out sulfo methylation of a phenols, an aldehyde and/or an aldehyde donator, and the initial condensate (B) by the sulfo methylation agent.

5. the initial condensate (A) with an amino ***** monomer, an aldehyde, and/or an aldehyde donator, and the initial condensate (B) with a phenols, an aldehyde, and/or an aldehyde donator -- the bottom of presence of a sulfo methylation agent -- and the bottom of presence of an aldehyde and/or an aldehyde donator -- or carry out a copolycondensation without presence

6. [whether Condensation Reaction is Carried Out under Presence of Amino ***** Monomer, Aldehyde and/or Aldehyde Donator, and Sulfo Methylation Agent, and] The initial condensate (A) with an amino ***** monomer, an aldehyde, and/or an aldehyde donator by the sulfo methylation agent [whether the condensation reaction of the initial condensate (SA) of sulfo methylation, the phenols, the aldehyde, and/or aldehyde donator which carried out sulfo methylation is carried out under presence of a sulfo methylation agent, and] It is under presence of an aldehyde and/or an aldehyde donator, or the copolycondensation of the initial condensate (SB) of sulfo methylation which carried out sulfo methylation of a phenols, an aldehyde and/or an aldehyde donator, and the initial condensate (B) by the sulfo methylation agent is carried out without presence.

7. Make an amino ***** monomer, a phenols, an aldehyde, and/or an aldehyde donator live together, and carry out a copolycondensation under presence of a sulfo methylation agent.

It can add and a sulfo methylation agent can be made to react after a reaction before a reaction or in a reaction in each above-mentioned condensation or an above-mentioned copolycondensation reaction.

[0013] In the above-mentioned copolycondensation reaction, although the addition proportion of an amino ***** monomer and a phenols is arbitrary, it is usually added 0.01-100 mols of phenols to one mol of amino ***** monomers. In the above-mentioned condensation or a copolycondensation reaction, it sets for an amino ***** reaction. in the case of amino ***** and the initial condensate (A) of an aldehyde The addition of the aldehyde to one mol of amino ***** monomers, and/or an aldehyde donator Usually, the about 0.5 to 2.0 times [of the number of reactant amino groups which can react with the aldehyde contained in one mol of these ***** system compound monomers] number of mols is suitable. For example, in the case of a urea, in the case of 1.0-3.0 mols and a melamine, the addition of an aldehyde and/or an aldehyde donator is about 1.5-6 mols.

[0014] When condensation resin is used for amino ** of this invention as an object for adhesives, a urea and/or a melamine are usually used as an amino ***** monomer. When using both a urea and a melamine, 1-6 mols of ureas are usually added to one mol of melamines, and an aldehyde and/or about 1-10 mols of aldehyde donators are added. The addition of an aldehyde [as opposed to one mol of phenols in the case of a phenols and the initial condensate (B) of an aldehyde] and/or an aldehyde donator is 0.2-3 mols. Moreover, 150/[1/100 of the number of sum mols of an amino ***** monomer and a phenols -] 100 considerable amount is usually suitable for the addition of a sulfo methylation agent.

[0015] In condensation of the above-mentioned initial condensate (A) and an initial condensate (B), or the copolycondensation reaction of an initial condensate (A) and an initial condensate (B), from the beginning of a condensation reaction, the whole quantity, in addition ** of an aldehyde and/or an aldehyde donator are good, and they may carry out split addition or per-continuum instillation.

[0016] Moreover, in the above-mentioned condensation or a copolycondensation reaction, a reaction is usually carried out in the domain of pH 4-12, and a catalyst or a pH regulator is added if needed. As these catalysts or a pH regulator, it is inorganic and organic an acid, alkali, or those salts, and caustic alkali of sodium, a caustic potash, a barium hydroxide, a calcium hydroxide, sodium carbonate, lime, ammonia, a trimethylamine, a triethylamine, a hexamethylenetetramine, a pyridine, a hydrochloric acid, oxalic acid, formic acid, an acetic acid, a lactic acid, a way acid, etc. are illustrated. Moreover, the addition of a catalyst or a pH regulator is usually several percent or less of an amino ***** monomer or a phenols. The reaction temperature of the above-mentioned condensation or a copolycondensation is usually 50-120 degrees C, and is performed about 0.5 to 48 hours. Furthermore, if required in addition to a catalyst or a pH regulator, a solvent, a complexing agent, and a third component can be added and this condensation reaction can be made to carry out in the above-mentioned condensation or a copolycondensation reaction.

[0017] if a part or all of a phenols that is added in this invention is made into a polyhydric phenol and it is [the copolycondensation object (C) with the high reactivity with an aldehyde is obtained and] required -- an acid catalyst and/or an aldehyde curing agent -- adding -- ordinary temperature -- or it hardens by low-temperature heating comparatively, and

hardening resin is excellent in a deck watertight luminaire, boiling-proof, and weatherability, and has strong adhesive ability, such as wood. To such a purpose, a resorcinol and the sulfo methylation object (SC) of a copolycondensation object (C) which especially the alkyl resorcinol is effective, uses together an alkyl resorcinol independent or 1 ** phenol, and an alkyl resorcinol as a phenols, carries out a copolycondensation to an amino ***** monomer, and/or amino ***** and the initial condensate of an aldehyde (A), and is obtained are especially desirable. Rather than it carries out the addition copolycondensation of both simultaneously with a monomer, in case a copolycondensation object (C) is manufactured, when using together 1 ** phenol and a polyhydric phenol (1) A polyhydric phenol under an aldehyde or aldehyde donator presence to the initial condensate of 1 ** phenolaldehyde which carried out sulfo methylation Or the initial condensate (SB), the amino ***** monomer, and/or amino ***** and the aldehyde condensate which carried out the copolycondensation without presence (A) under an aldehyde and/or aldehyde donator presence or [whether a copolycondensation is carried out without presence, and] (2) The initial condensate (SB) of 1 ** phenolaldehyde, the amino ***** monomer, and/or amino ***** and the aldehyde condensate (A) which carried out sulfo methylation under an aldehyde and/or aldehyde donator presence in or the copolycondensation object (SC) condensed without presence. Furthermore, although there is the technique of being under an aldehyde and/or aldehyde donator presence, or carrying out the copolycondensation of the polyhydric phenol without presence etc., since a more stable copolycondensation object is obtained, the former technique (1) is the desirable copolycondensation technique.

[0018] Generally, it is obtained that a product [carry / to the methylol machine produced in the condensate of a phenols and an aldehyde] is more stable rather than it performs sulfo methylation to the methylol machine produced in the condensate of amino ***** and an aldehyde.

[0019] Heating hardening will be carried out if the acid catalyst 0.05 - 10 weight section, and the curing agent 0 which will consist of an aldehyde donator like para ***** if required - 50 weight section are added to amino ***** , the phenols, and the aldehyde copolycondensation object (SC) 100 weight section by which sulfo methylation of the [hardening of initial copolycondensation object by which sulfo methylation was carried out] this invention was carried out. The heating hardening is performed at low temperature farther than the case (they are usually 1 minute / about 1mm at 125-140 degrees C in plywood adhesion) of hardening of resol type phenol resin, and they are usually 0.5 - 1 minute / about 1mm at 110-120 degrees C. If the curing agent which the reactivity with the aldehyde of this copolycondensation resin (SC) will be raised notably, and will consist of an aldehyde donator like para ***** if a polyhydric phenol like a resorcinol or an alkyl resorcinol exists in the phenols component of the copolycondensation resin (SC) with which sulfo methylation of this invention was carried out is added, it is not concerned with an acid and alkaline situation, but comes to be able to carry out a room temperature setting in large pH field. However, it is required to heat in the ordinary temperature [like a hexamethylenetetramine] whose aldehyde donator is, more than the decomposition temperature, in being stable. Moreover, in this invention, even if it adds an acid or alkaline curing catalyst in the case of hardening, it does not interfere. The acid or alkaline above-mentioned curing catalyst If it illustrates, an ammonium chloride, an ammonium sulfate, an ammonium acetate, an ammonium thiocyanate, imido sulfonic-acid ammonium, ammonium phosphate, an ammonium oxalate, a hexamethylenetetramine, ammonia, sodium acetate, a sodium phosphate, an aniline chloride, An ammonium sulfate, a hydrochloric acid, oxalic acid, formic acid, an acetic acid, a lactic acid, a way acid, and the carboxylates like oxalic acid dimethyl ester Organic halogenides, such as the acid-anhydrides [, such as a maleic-acid anhydride and a phthalic-acid anhydride], specific-salt [of monochloroacetic acid], alpha, and alpha'-dichlorohydrin, There are urea adducts, such as a hydrochloride of aminess, such as an ethylamine hydrochloride and a triethanolamine hydrochloride, a salicylic-acid urea adduct, a stearin acid urea adduct, and an oenanthic-acid urea adduct, an N-trimethyl taurine, etc., and these may use together a kind or two sorts or more. If required in the case of hardening, furthermore, amino resins, such as 1 ** phenol system resin, a polyhydric-phenol system resin, a urea system resin, and a melamine system resin, Synthetic rubber, such as natural rubber and its derivative, a styrene butadiene rubber, acrylonitrile-butadiene rubber, chloroprene rubber, ethylene-propylene rubber, polyisoprene rubber, and isoprene-isobutylene rubber, The homopolymer of vinyl monomers, such as vinyl acetate, a propionic-acid vinyl, styrene, acrylic ester, methacrylic ester, acrylonitrile, an acrylic acid, a methacrylic acid, a maleic acid, a vinyl chloride, a vinylidene chloride, and a ***** pyridine Or two or more sorts of copolymers of these vinyl monomers, Emulsions, and ***** or the aqueous solutions of various synthetic resin, such as polyurethane, a polyamide, an epoxy resin, a butyral resin, polyethylene, polypropylene, a vinyl acetate-ethylene copolymer, a chlorinated polyethylene, chlorination polypropylene, and polyester, Moreover, water soluble polymers and natural gums, such as polyvinyl alcohol, a sodium alginate, a starch, a starch derivative, glue, gelatin, powdered blood, a methyl cellulose, a carboxymethyl cellulose, a hydroxyethyl cellulose, a polyacrylic acid, and a polyacrylamide, Furthermore, bulking agents, such as carbonic acid calcium, talc, plaster, carbon black, wood flour, walnut powder, coconut shell powder, a wheat flour, and rice powder, A pigment, a color, a flame retarder, a flame proofing agent, an insecticide, antiseptics, an antioxidant, an ultraviolet ray absorbent, DBP, DOP, Third components, such as plasticizers, such as a ***** acid ester system plasticizer like a dicyclohexyl free-wheel-plate rate and other tricresyl phosphate, may be added in this copolycondensation object (SC), and this copolycondensation object (SC) may be made to denaturalize by the copolycondensation, mixture, etc.

[0020]

[Function] Amino ** of this invention the sulfo methylation object (SC) of condensation resin (C), i.e., amino ***** , a phenols, and an aldehyde copolycondensation object

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